(19) **Japanese Patent Office** (JP)
(12) **Official Gazette for Unexamined Patent Applications** (A)

(11) Japanese Patent Application Kokai Publication No. H04-298038
(43) Publication Date: October 21, 1992
Number of Claimed Inventions: 1 (total of 3 pages)
Request for Examination: Not requested

(51) International Class.[5]	Identification No.	JPO File No.	FI	Indication of Technology
H 01 L 21/304	341	V 8831-4M		
		L 8831-4M		

(21) Application No.: H03-063167
(22) Application Date: March 27, 1991

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Specifications

(54) <Name of Invention>

Cleaning Method for Wafer

(57) <Abstract>

<Purpose>

This invention introduces a cleaning method for semiconductor wafers with the purpose of obtaining high quality wafers by improving the method for the removal of foreign matter that has adhered to the surface of semiconductor wafers.

<Constitution>

Once the surface of a semiconductor wafer undergoes oxide film formation while being held within an ozone atmosphere, it is then dipped into a reducing solution in order to remove the oxide film, resulting in a cleaning operation in which foreign matter such as heavy metals, etc., that have adhered to the wafer surface are removed.

<Effect>

This invention makes it possible to remove foreign matter from the surface of a wafer within an atmosphere of normal temperature and normal pressure without degrading the surface conditions of the wafer, which in turn makes it possible to obtain high-quality wafers at a favorable yield level.

<Claims>

<Claim 1>

A cleaning method for a semiconductor wafer is characterized by the fact that said wafer undergoes oxide film formation along its surface while being held within an ozone atmosphere, after which it is dipped into a reducing solution in order to remove the oxide film, resulting in a cleaning operation in which foreign matter that has adhered to the wafer surface is removed.

<Detailed Description of the Invention>

<0001>

<Industrial Field of Application>

This invention is related to a manufacturing process for semiconductor wafers, particularly as it pertains to an improvement in the cleaning method applied to these wafers.

<0002>

<Prior Art>

When contaminants make contact with the surface of semiconductor wafers, this can cause a drop in the useful properties of the wafers, and this is why it is necessary to remove these contaminants. Forms of contaminants include foreign matter (dirt), heavy metals, etc., that adhere to the surface. The adhesion strength is particularly high in the case of heavy metals, which is why they are not easy to remove. For example, one method for cleaning Si wafers is called the RCA cleaning method, which is known to leave residual amounts of Fe and Al, which are used because of their ability to remove heavy metals such as Cu, Zn, etc.

<0003>

An etching method is used as a means for reliably removing these substances. For example, in the case of GaAs wafers, a sulfuric acid based etching liquid (a mixture of H_2SO_4, H_2O_2, and H_2O) or an ammonia based etching liquid (NH_4OH, H_2O_2, and H_2O) can be used in order to remove several μm of contaminants from the surface. However, when this method is used, waviness or pitting may occur on the surface, causing a loss of flatness along the surface.

<0004>

Although there is also a dry etching method which uses plasma, etc., this provides only a small removal effect and may end up forming a distorted layer on the surface.

<0005>

An example of a method that has been introduced for removing foreign matter without harming the flatness or crystal properties is one in which a thermal oxide film is formed on the surface, after which the wafer is heated within a vacuum in order to remove the oxide film (Saito, et al.: Technical Reporting Committee of the Electronic Telecommunications Association, ED-117, 1987, P. 43). This method was proposed as a pre-treatment for MBE (Molecular Beam Epitaxial Method) and has been used in the cleaning of GaAs wafers. In short, the wafer undergoes heat oxidation at 450°C to form an oxide film with a thickness of 100 – 200 Å (Angstrom), after which the wafer is heated to at least 750°C within a vacuum in order to remove the oxide film. Based on this method, a remarkable removal effect can be confirmed in which the carbon density of the surface is reduced to one third.

<0006>

<Problem to be Solved by the Invention>

As noted above, it has been shown that prior etching methods end up degrading the surface condition of wafers. Furthermore, although the method for removing a heat oxide film is superior as a treatment immediately prior to epitaxial growth, it is difficult to apply this method to the production of wafers. This is because of the heat treatment process that is required. Particularly in the case where a high temperature of 750°C or more is applied, this will end up creating defects in the wafers such as dislocation.

<0007>

In the case of compound semiconductors made from GaAs, InP, etc., As and P are volatile when heated within a vacuum, which will result in the transformation of the surface layer. Furthermore, treatments conducted within a vacuum are unfavorable from the standpoint of production. Finally, when a thermal oxide film is formed, the make-up of the oxide film can end up changing according to the atmosphere, temperature, etc., and as a result, the volatility temperature may also change, resulting in a loss of repeatability.

<0008>

The purpose of this invention is to introduce a cleaning method for a wafer in which it becomes possible to resolve the shortcomings of the prior art examples noted above by removing foreign matter from the surface of a wafer within an atmosphere of normal temperature and normal pressure without degrading the surface conditions of the wafer.

<0009>

<Means for Solving the Problem>

In order to resolve the issues noted above, the constitution of the method described in this invention for the cleaning of wafers is as follows. Once the surface of a semiconductor wafer undergoes oxide film formation while being held within an ozone atmosphere, it is then dipped into a reducing solution in order to remove the oxide film, resulting in a cleaning operation in which foreign matter that has adhered to the wafer surface is removed.

<0010>

<Operation>

A method is conducted in which an oxide film is formed onto a semiconductor wafer surface while the wafer is being held in an ozone atmosphere at normal temperature. Then, a reducing solution comprised of hydrofluoric acid, etc., is used as a method for removing this oxide film. Besides hydrofluoric acid, other solutions with this type of reduction capability include hydrochloric acid, nitric acid, and sulfuric acid or a diluted form thereof. In addition, alkaline solutions with a pH of 12 or higher are effective due to the fact that they can dissolve the oxide As within GaAs.

<0011>

<Embodiment>

The following is an explanation of a testing method, including the results of the test, in which case an oxide film is formed on a GaAs wafer surface, after which the film is removed and a measurement is conducted in order to determine the concentration of the residual heavy metals.

<0012>

The samples used for this test are semi-insulated GaAs wafers measuring 75 mm in diameter, in which case the surfaces of the wafers have undergone a mirror finishing process. Four wafers are used, with one wafer set aside for the purpose of measuring the initial surface contamination level. The other three wafers are used in the cleaning test.

<0013>

An EYE Ozone [Iozone?] device (made by Iwasaki Electric Co., Ltd.) is used in order to create the ozone atmosphere. In short, once a wafer is placed inside this device, an ultraviolet light of 15 mW with a wavelength of 245 nm is irradiated against the wafer. This causes ozone to be generated near the wafer, such that the wafer surface is oxidized to the point that an oxide film is formed. The thickness of the oxide film is measured using an ellipsometer. The film thickness of the initial sample is measured at 12 Å. The wafer is placed into the aforementioned device, and the film thickness formation time is set to 0 – 240 min in order to create a film with a thickness of 12 – 210 Å.

<0014>

This wafer is then dipped into a diluted solution of hydrofluoric acid ($HF : H_2O = 50 : 1$) for two minutes, and once the oxide film is removed, the wafer is rinsed with purified water for five minutes (at a flow rate of one liter per minute) and then dried.

<0015>

The oxide film thickness after cleaning is 7 – 9 Å, and thus according to the aforementioned treatment, it is confirmed that the oxide film has been removed. Furthermore, it is confirmed that there is no evidence of waviness, dullness, or pitting along the surface of the wafer after the treatment, which indicates that a favorable mirror surface has been achieved.

<0016>

Next, a measurement is conducted in order to determine the residual amount of heavy metals. The method used for this measurement is explained below.

<0017>

First, an etching liquid (ammonia based) is applied in drops (0.5 cc) onto the wafer surface, and after a specified amount of time has elapsed, the liquid is recovered, and a measurement is conducted using the atomic absorption method in order to determine the concentration of heavy metals within the liquid.

<0018>

A measurement has been taken previously for the concentration of heavy metals within the etching liquid, and based on the difference between this and the recovered liquid, as well as the area of the etching liquid at the time it was applied to the surface, a calculation is conducted in order to determine the adhesion amount per unit of area according to the etching liquid. This is repeated until there is no difference between the recovered liquid and the etching liquid, at which time the data is integrated in order to arrive at a surface adhesion amount. At this point, the metals that are measured are Cu, Cr, Fe, and Zn.

<0019>

Figure 1 is a graph of the test results for the embodiment of this invention. Based on the aforementioned test, the x-axis represents the oxide film thickness (Å), and the y-axis represents the concentration of the residual heavy metals.

<0020>

As shown in Figure 1, the adhesion amount for each heavy metal declines as the film thickness increases up to 100 Å, confirming the removal effect. The adhesion amount becomes nearly constant from the point where the film thickness exceeds 100 Å. At this point, the concentration of each heavy metal has been reduced by one digit when compared to the initial values, thus making it clear that a significant amount of removal has been achieved.

<0021>

Based on this embodiment, it has become possible to remove heavy metal contaminants from a semiconductor wafer surface, and an improvement in production yields can thus be anticipated.

<0022>

An electric discharge method may also be used as a means for creating an ozone atmosphere. With regard to the removal of the oxide film, it is also acceptable to use a method in which the samples are held within a steam generated from a reduction liquid.

<0023>

Furthermore, the semiconductor wafer that is used can be a compound semiconductor made from a substance other than GaAs, such as InP, GaP, InAs, etc.

<0024>

<Effect of the Invention>

This invention makes it possible to easily obtain wafers with favorable surface conditions due to an extremely low adhesion amount of heavy metal contaminants as well as an absence of dullness, waviness, or pitting along the surface. In short, due to the fact that high quality wafers can be obtained at high yields through the use of this invention, it can make a significant contribution to the increase in profitability.

<Simple Explanation of the Drawing>

<Figure 1>

This is a graph that shows the relationship between the oxide film thickness and the residual heavy metal concentration as described in the embodiment of this invention.

<Figure 1>

[y-axis:] Residual Heavy Metal Concentration (cm^{-2})

[x-axis:] No Treatment Oxide Film Thickness (Å)

(19)日本国特許庁（JP）　(12) 公開特許公報(A)　(11)特許出願公開番号

特開平4－298038

(43)公開日　平成4年(1992)10月21日

(51)Int.Cl.⁵	識別記号	庁内整理番号	F I	技術表示箇所
H01L 21/304	341 M	8831－4M		
	L	8831－4M		

審査請求　未請求　請求項の数1（全 3 頁）

(21)出願番号　特願平3－63167

(22)出願日　平成3年(1991)3月27日

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(54)【発明の名称】　ウエハの洗浄方法

(57)【要約】

【目的】半導体ウエハの表面に付着した異物を除去する方法を改善して、高品質のウエハを得ることを目的とした半導体ウエハの洗浄方法を提供するものである。

【構成】半導体ウエハをオゾン雰囲気中に保持して、その表面に酸化膜を形成した後、これを還元性溶液に浸漬してその酸化膜を除去することにより、ウエハ表面に付着した重金属等の異物を除去洗浄する。

【効果】本発明により、ウエハの表面状態を悪化させることなく常温、常圧の雰囲気中で表面の付着物を除去することができ、高品質のウエハを歩留まりよく得ることができるようになった。

【0016】これらのウエハ表面に残留している重金属の量を測定した。測定法は以下の通りである。

【0017】まず、ウエハ表面にエッチング液（アンモニア系）を適下（0．5cc）し、所定時間保持した後、液を回収し、その液中の重金属の濃度を原子吸光法によって測定した。

【0018】予めエッチング液の重金属の濃度を測定し、回収液との差および表面に適下した時のエッチング液の面積から、エッチング液に取り込まれた単位面積当りの付着量を算出した。これを回収液とエッチング液との差がなくなるまで繰返し、データを積算し、表面付着量とした。この際、測定した金属はCu、Cr、Fe、Znである。

【0019】図1は本発明の実施例の実験結果図である。すなわち、上記の実験において、酸化膜厚（Å）を横軸に、残留重金属濃度を縦軸にとって表示した図である。

【0020】図1において、各重金属共に、膜厚が100Åまでは厚さにしたがって、付着量は減少し、除去効果が認められる。膜厚が100Å以上になると付着量はほぼ一定値となる。この時、各重金属濃度は、初期値よりも1桁減少しており、大幅に除去されたことがわかる。

【0021】本実施例により、半導体ウエハ表面の汚染重金属を除去することができ、製品歩留まりの向上が期待できる。

【0022】オゾン雰囲気を生成する方法として、放電による方法でもよい。酸化膜除去方法として、試料を還元液の蒸気中に保持する方法でもよい。

【0023】また、対象となる半導体ウエハとしてはGaAs、のほかにInP、GaP、InAs等の化合物半導体がある。

【0024】

【発明の効果】本発明によれば、汚染物重金属の付着量が極めて少なくかつ、表面にくもり、うねり、ピット等がなく、表面状態の良好なウエハを容易に得ることができる。すなわち、本発明により、高品質のウエハが歩留まりよく得られるので経済性の向上におおいに貢献することができる。

【図面の簡単な説明】

【図1】本発明の一実施例の酸化膜厚と残留重金属濃度の関係図である。

【図1】